

Crucial Role of V in $\text{La}_2\text{Ni}_x\text{V}_{1-x}\text{O}_{4+\delta}$ Catalyst for Selective Oxidation of Propane

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Introduction

Selective oxidation of light alkane to olefins and oxygenates over metal oxide catalysts is still far away from industrial application because the yields obtained are too low due to secondary deep oxidation reactions. Tuning the activity of surface oxygen, the selectivity to olefins and oxygenates can be enhanced. In this respect mixed oxides, which are able to easily release oxygen without changing the lattice structure, are considered as promising catalysts [1].

In this study the relation between reduction degree of $\text{La}_2\text{Ni}_x\text{V}_{1-x}\text{O}_{4+\delta}$ catalyst and selectivity in propane conversion is reported. The role of V in enhancing the selectivity toward propylene is discussed.

Materials and Methods

The reducibility of the catalysts and consequent removability of oxygen active species was investigated by H_2 -TPR analysis within 25-980°C. The oxygen surface sites were probed by pulsing propane over the catalyst surface at 550°C (titration test).

Results and Discussion

The reduction profile of $\text{La}_2\text{NiO}_{4+\delta}$ in H_2 has shown 2 distinctive reduction steps at around 300 and 650°C, which were addressed to interstitial oxygen removal and to complete reduction of Ni^{2+} to Ni^0 , respectively. V-doped $\text{La}_2\text{NiO}_{4+\delta}$ showed similar two peaks reduction profile but a consistent shift toward higher reduction temperature was observed. For interstitial oxygen the shift was larger than for oxygen related to Ni^{2+} reduction. Thus, V stabilizes the oxygen species under reducing conditions, which is a crucial issue in selective oxidation of propane.

In case of propane pulse experiments at 550°C only interstitial oxygen can be activated. Products distributions during subsequent propane pulses over $\text{La}_2\text{NiO}_{4+\delta}$ and V-doped $\text{La}_2\text{NiO}_{4+\delta}$ are shown in Fig. 1 and 2, respectively. Fresh samples, $\text{La}_2\text{NiO}_{4+\delta}$ and V-doped $\text{La}_2\text{NiO}_{4+\delta}$, showed relatively high conversion of propane. Mainly CO_2 and H_2O were observed as products testifying the oxygen removal from the catalyst. With further depletion of oxygen, for both catalysts the propane conversion and formation of CO_2 decreases, and production of C_3H_6 , C_2H_4 , CH_4 and H_2O (dehydrogenation and cracking products) became predominant. At this stage the catalysts showed the highest selectivity toward propylene. Continuing with the propane pulses, the oxides performance became different. For un-doped $\text{La}_2\text{NiO}_{4+\delta}$, after few extra pulses, the conversion immediately increases and the products distribution turned towards coking (coke, CH_4 and CO additionally). In the case of V-doped $\text{La}_2\text{NiO}_{4+\delta}$, both conversion and products distribution remarkably remained constant (dehydrogenation and cracking

products). There is a window in reduction degree of V-doped $\text{La}_2\text{NiO}_{4+\delta}$ in which selectivity to olefins is very promising for further application in selective oxidation.

After titration test both materials were regenerated with oxygen pulses. The regeneration process also evidenced that only part of interstitial oxygen is responsible for catalysts activity at 550°C.

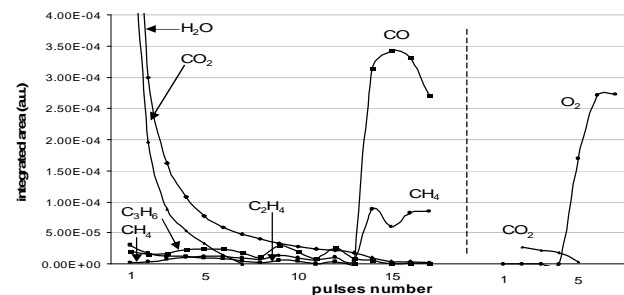


Figure 1: Zoom in on the products distribution during the titration test on $\text{La}_2\text{NiO}_{4+\delta}$ at 550°C (left hand side) and regeneration profile of the catalyst by O_2 pulse (right hand side).

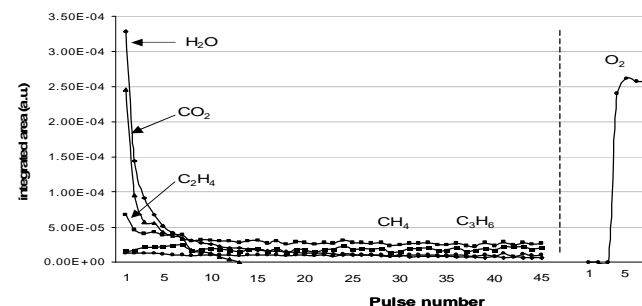


Figure 2: Products distribution during titration test (45 pulses) of $\text{La}_2\text{Ni}_{0.9}\text{V}_{0.1}\text{O}_{4+\delta}$ at 550°C (left hand side) and regeneration profile of the catalyst by O_2 pulse (right hand side)

Significance

Tuning of oxygen activity by doping metal can provide an extended window in the operation conditions in which enhanced selectivity to propylene can be achieved. Applying such materials in a catalytic dense membrane reactor is promising if oxygen mobility and reactivity are in a proper balance.

References

1. A. Chetouani, B. Taouk, E. Bordes-Richard, *Catalysis Today* 91-92, 73 (2004)